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The investigation of chemical reactions in the supercritical region of water requires a knowledge of the thermodynamic quantities (K , ΔH° , ΔS° , and ΔC_p°) associated with water dissociation and solute-solute interaction in this region. In this study, these quantities have been determined to 350 or, in some cases, to 370°C for water ionization and alkali and alkaline earth-chloride ion interaction. The determinations were made using a high precision flow calorimeter designed and constructed to withstand the corrosive and high temperature conditions encountered in the study. The results are consistent with a model involving water molecules as active participants in the reactions. As temperature increases, the percentage of water molecules participating in hydrogen bonding decreases with resulting large effects on ΔH° , ΔS° , and ΔC_p° values for chemical reactions. The K and ΔH° values provide essential information for the design of processes intended to operate under supercritical water conditions.

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**CALORIMETRIC STUDY OF IONIZATION AND OXIDATION REACTIONS
IN SUPERCRITICAL WATER**

FINAL PROGRESS REPORT

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March 25, 1997

U.S. ARMY RESEARCH OFFICE

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I. Final Progress Report

A. Statement of the Problem Studied

Understanding chemical reactions that occur in the water critical region requires a knowledge of the equilibrium constants (K) for solute-solute interactions in aqueous solutions. In addition, the nature of solute-solvent interactions must be understood since the structure and properties of water show large changes in the critical region. The thermodynamic quantities ΔH° , ΔS° , ΔC_p° give insight into both the solute-solute and solute-solvent interactions.

The problem studied involved the measurement using flow calorimetry of K , ΔH° , ΔS° , and ΔC_p° values for selected chemical reactions from 320 to 370°C. The corrosive nature of aqueous solutes in this temperature region and the effect of high temperature on the lifetime and performance of calorimeter components required the design, construction, and evaluation of a new calorimeter.

B. Summary of the Most Important Results

The study has resulted in the construction of a new calorimeter capable of operation from 250 to 450°C, the development of an improved model for solute-solvent interactions at high temperatures, the determination of consistent ΔH° values for water ionization in the water critical region, and the demonstration that accurate heat of dilution values can be used to determine K , ΔH° , and ΔS° values for solute ionization. These results are now summarized.

1. New Calorimeter

This calorimeter and its performance have been described in a recent publication by us (Section C, b). This calorimeter has worked well up to 370°C. The reacting fluids come in contact with only platinum alloys and gold at the high temperatures and platinum alloys, gold, teflon, titanium, and monel at room temperature. The interior of the calorimeter has had excellent resistance to corrosion and leaks, but the joints between the lead wires and the electrical heaters on the exterior of the heated vessels and tubes have failed several times. At first, these joints were silver brazed. When the silver brazed joints failed, they were replaced with welded joints, which exhibited improved corrosion resistance, but they still corroded at the high temperatures. We are replacing these components with platinum alloy heaters with gold leads. These are joined by gold brazing. The total assembly is expected to be corrosion resistant. Since these leads are not exposed to corrosive chemicals they should allow routine operation at temperatures up to 450°C.

2. Model for Solute-Solvent Interactions at High Temperature

The effect of solute-solvent interactions on thermodynamic quantities for ionic reactions in aqueous solution has been discussed in two of our publications (Section C, a,c). At elevated temperatures, $\log K$ increases with temperature for all simple ion association reactions (the opposite is usually observed for ion association reactions at ambient conditions). The ΔH° and ΔS° values provide the explanation for this increase in $\log K$. Both ΔH° and ΔS° values become progressively more positive as temperature increases. However, the increase in $T\Delta S^\circ$ is larger than the increase in ΔH° , making ΔG° values more negative as temperature increases. Since the favorable entropy effect is greater than the unfavorable enthalpy effect, the large positive ΔS° is the driving force for ion association in high temperature aqueous solutions. The large positive values

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of ΔH° and ΔS° for ion association reactions can be explained by solvation effects. The disruption of hydrogen bonding at high temperatures results in increased numbers of degrees of freedom for the water molecules in the bulk phase. As temperature increases, the extent of hydrogen bonding in water decreases, the dielectric constant of water decreases, and the number of water molecules in the solute hydration sphere increases. The water molecules in the hydration sphere have lower enthalpies and entropies than the water molecules in the bulk phase. When ion association occurs, many water molecules are released from the hydration sphere to the bulk phase. A considerable amount of energy is required to restore the released water molecules to the rotational, vibrational, and translational freedom which molecules have in the bulk water. The energy required in this process far exceeds the energy released by the bond formation between the ions. The absorption of the required energy from the surroundings results in the large positive ΔH° values. The large positive ΔS° values result from ion association because many water molecules are released from the highly ordered structure of the hydration sphere of the ions to the less ordered state of the bulk water. The solvent effects become increasingly significant as temperature increases. The ΔH° , ΔS° , and ΔC_p° values associated with solute-solute interactions as temperature increases provide valuable insight into these solute-solvent interactions.

3. Heat of Ionization of Water at High Temperature

The ionization of water is involved in most chemical reactions at high temperatures. A knowledge of the thermodynamic quantities associated with this reaction is essential for the understanding of hydrolysis and other reactions in high temperature aqueous systems. We have published a calorimetric study of water ionization to 350°C (Section C, d). This study is important because it provides accurate thermodynamic data for a temperature region where these data were not known earlier. It also provides a base for the investigation of water ionization through the water critical region.

4. Determination of Thermodynamic Quantities from Heat of Dilution Data

We have measured heats of mixing of H₂O with solutions of HCl, KOH, KCl, NaCl, NaOH, LiCl, CsCl, CsOH, BaCl₂, CaCl₂, and MgCl₂ up to 350 or 370°C and at pressures of 11.0 to 25.5 MPa. These heat of dilution data have been used to calculate Pitzer activity coefficients as a function of temperature for these systems and to determine the log K and ΔH° values for the dissociation of the above acids, bases, and salts up to temperatures of 350°C. In addition, heats of mixing of HCl and KOH have been measured to 370°C and 25.5 MPa. From the results, log K and ΔH° values have been determined for water ionization. Calculation of thermodynamic quantities for reactions at 370°C and at higher temperatures requires the full development of the model based on Helmholtz energy.

Heat of dilution data for LiCl, KCl, and CsCl at 300, 325, and 350°C have been used to determine thermodynamic quantities for the dissociation of these three salts. A manuscript reporting these results has been published (Section C, e). This work demonstrates that reliable values for K , ΔH° , ΔS° , and ΔC_p° can be calculated from heats of dilution for associated species. The ability to determine these quantities from heats of dilution will be valuable at higher temperatures, especially in those cases where mixing of reactants to form the desired species may be difficult to accomplish due to the introduction of additional reactions and possible undesirable side reactions.

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such as precipitation.

C. List of Publications and Technical Reports

1. The following publications resulted from work on the Grant.

a. Oscarson, J.L.; Izatt, R.M.; Gillespie, S.E.; Chen, X.; Cao, H. "The Importance of Chemical Speciation in Near and Super-Critical Aqueous Solutions"; *Proceedings of the First International Workshop on SuperCritical Water Oxidation, Supercritical Water Oxidation: A Revolutionary Environmental Technology*, February 6-9, 1995, Amelia Island, Florida.

b. Chen, X.; Oscarson, J.L.; Cao, H.; Gillespie, S.E.; Izatt, R.M. "A New Flow Calorimeter Designed for Operation to 450°C and 50 MPa"; *Thermochimica Acta*, 1996, 285, 11-23.

c. Izatt, R.M.; Oscarson, J.L.; Gillespie, S.E.; Chen, X.; Wang, P.; Watt, G.D.; "A Calorimetric Study of Ligand Interactions with Protons and Metal Ions in the 100 to 400°C Range"; *Pure Appl. Chem.*, 1995, 67, 543-549.

d. Chen, X.; Oscarson, J.L.; Gillespie, S.E.; Cao, H.; Izatt, R.M. "Determination of Enthalpy of Ionization of Water from 250 to 350°C"; *J. Solution Chem.*, 1994, 23, 747-768.

e. Gillespie, S.E.; Chen, X.; Oscarson, J.L.; Izatt, R.M. "Enthalpies of dilution of aqueous solutions of LiCl, KCl, and CsCl at 300 to 350°C"; *J. Solution Chem.*, 1997, 26, 47-61.

f. Chen, X.; Izatt, R.M.; Oscarson, J.L. "Thermodynamic Data for Ligand Interaction with Protons and Metal Ions in Aqueous Solutions at High Temperatures"; *Chem. Rev.*, 1994, 94, 467-517.

2. Interim progress reports were submitted for each of the first two years of the Grant.

D. Listing of Reportable Inventions

None

E. Listing of Participating Scientific Personnel

1. Reed M. Izatt, Principal investigator
2. John L. Oscarson, Co-Principal investigator
3. Hongjie Cao, Post-doctoral
4. Xuemin Chen, Post-doctoral
5. Sue E. Gillespie, Research technician